AN INVESTIGATION INTO BIMETALLIC HOLLOW NANOPARTICLES IN CATALYSIS

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AN INVESTIGATION INTO BIMETALLIC HOLLOW NANOPARTICLES IN CATALYSIS

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SUMMARY

Nanocatalysis, catalysis using particles on the nanoscale, is an emerging field that has tremendous potential. Nanoparticles have different properties than bulk material and can be used in different roles. Macro sized precious metals, for example, are inert, but nanoparticles of them are becoming more widely used as catalysts. Understanding the manner in which these particles work is vital to improving their efficacy.

This thesis focuses on two aspects of nanocatalysis. **Chapter 1** begins with a brief introduction into nanotechnology and some of the areas in which nanoparticles are different than bulk particles. It then proceeds into an overview of catalysis and nanocatalysis more specifically. Focus is brought to the definitions of the different types of catalysis and how those definitions differ when applied to nanoparticles. **Chapter 2** is in finding an inert support structure to more easily assist in recycling the nanoparticles. Polystyrene microspheres were studied and found to prevent platinum nanoparticles from aggregating in solution and possibly aid in recycling of the nanoparticles. These nanoparticles were used in catalysis, aiding in the reduction of 4-nitrophenol in the presence of sodium borohydride. While the rate decreased by a factor of ~ 7 when using the polystyrene, the activation energy of the reaction was unaltered, thus confirming the inactivity of the polystyrene in the reaction.

In **Chapter 3**, nanocatalysis was studied by examining bimetallic hollow nanoparticles with specific attention to the effect of altering the ratios of the two metals. Ten different bimetallic nanocages were tested in an electron transfer reaction between hexacyanoferrate and thiosulfate. Five PtAg nanocages and five PdAg with

varying metal ratios were prepared and studied. It was found that while silver cubes immediately precipitate out of solution when combined with thiosulfate, a small amount of either platinum or palladium allows the particles to remain in solution and function as a substantially more effective catalyst. However, as additional Pt was added the activation energy increased.

To obtain a better understanding of the catalysis using bimetallic cages, the evolution of these cages was studied as the 2^{nd} metal was added. Initially the particle edge length increased and then slowly decreased back to the size of the template cubes. The increase in edge length suggests of addition of material to the nanoparticles. This indicated the 2^{nd} metal is on the outside of the cage, which was confirmed using UV-Vis spectroscopy and EDS mapping. By understanding how these bimetallic particles evolve, we may be able to manipulate these synthetic methods to more precisely design nanoparticles for catalysis.

CHAPTER I

INTRODUCTION

1.1 Nanochemistry Overview

Nanochemistry, the study of the chemical properties of particles and their structures of sizes between 1 and 100 nanometers, has seen an impressive growth in both research and applications over the past fifteen years. The real world uses have extended into the field of medicine where silver nanoparticles are used for their anti-microbial properties. Nanochemistry has become an important subdivision of chemistry in the past few decades, with applications in cancer therapeutics[10, 14, 6], plasmonics[11], and energy[8, 15], among others. Precious metals in particular are being studied for their potential applications in many fields raging from medicine to sensing and optics. Gold and silver are largely inert when used as bulk materials (thus the term noble metals), but are effective as catalysts[] and show promise in cancer treatment when they are reduced to sub micron sizes[5]. While research in nanochemistry has only begun to blossom in the past decade and a half, it has been in use for centuries, albeit unknown to those whom have manipulated it.

The properties of nanotechnology has been used for centuries in stained glass. The Sainte Chapelle in Paris is demonstrative of this effect, as are many of the other famous cathedrals and chapels in the world.[17] Another common example of the ever present use of nanoparticles is the Lycurgus Cup. Created in the 4th century AD, The Lycurgus Cup (Figure 1) has a different color depending on whether light is coming from within the cup versus light being shone on it. A green color is apparent when light is scattered at the exterior of the cup, but when a light is placed inside and the green color is absorbed, the remaining colors coming

through the glass appear red. This is because the light is scattered when outside the cup and is absorbed when the light is on the interior. This can be explained by the addition of silver nanoparticles to the glass, which appear different colors based on whether light is absorbed or scattered.

Figure 1: Lycurgus Cup demonstrating how gold nanoparticles are affected by scattering (A) and absorption (B) differently.

While this property, the ability of nanoparticles to strongly absorb or scatter light differently, has been used and manipulated for hundreds of years, it has only been recently understood. It wasn't until 1857 when Michael Faraday synthesized pure colloid gold solutions (which are, in effect, spherical gold nanoparticles of varying sizes), that a scientific undertaking of this effect had started. He could not measure the nanooparticle sizes at the time, but he believed the varying optical properties of the different gold solutions was due to the small size of the gold particles.[18] Faraday was correct, but proof of that would have to wait nearly half a century later until Gustav Mie, using Maxwell's equations, explained the origin of the brilliant colors of gold nanosphere solutions.[16]

The plasmonic field studied the unique properties and potential applications of gold and silver nanoparticles. Nanoparticles are capable of harnessing the energy of light by using surface plasmon resonance. Acting as a lens for the light, the nanoparticles focus the energy into a dimension much smaller than the wavelength of the light itself with much higher intensity than the light that created

it.[13] This high scattered light intensity is used in cancer diagnostics and when this high intensity is absorbed, it is converted rapidly into heat with promise in photothermally destroying tumors.[10] Plasmonics is a very active field in manipulating light in many new applications in photonics, sensing, and metamaterials. In chemistry, it has introduced new properties that are used in catalysis. Catalysis is of particular importance to the field of nanochemistry, given its role in the economy and the potential improvement using nanoparticles.

1.2 Nanoparticles in Catalysis

Nanocatalysis is an important subfield of nanotechnology. Catalytic processes contribute to fields which produce $900 billion a year in revenue. However, chemical processes in the U.S. also require approximately the same energy as 46 trillion gallons of gasoline, per annum.[7] There is therefore a great deal of economic incentive to reduce the energy expenditure. Nearly all industrial processes use a catalyst of some sort to increase production. In some cases, these processes are improved by orders of magnitude by the use of catalysts. One of the largest processes in the world, the Haber process, which produces fertilizer from hydrogen and nitrogen, uses magnetite to accelerate the reaction rate.[4] Catalytic converters, which are required on every car in the US, use platinum and palladium to convert carbon monoxide into the less poisonous carbon dioxide.[9] All of these industrial applications, however, use bulk catalysts. Nanocatalysis has shown improved catalytic activity compared to bulk catalysts. This is due to an increased number of active sites for the smaller versions of the catalysts as compared their larger counterparts.

The active sites on a catalyst are those areas which can induce catalysis. These active sites are usually found on the surface of the catalyst, primarily on the corners, edges, or at defect sites. The corners are the most active, followed by edges, and finally the faces of the catalyst specifically if they have defective sites.[7] The interior of a catalyst is inert and of no use to the reaction to which it is being applied. Nanoparticles have a high surface to volume ratio, which means they have more active sites (and a higher percentage of the more effective active sites), making them ideal catalysts. A nanoparticle with a diameter of 10 nm has approximately 45 % of its atoms on its surface, while a particle with a diameter of 100 nm has nearly a full order of magnitude fewer surface atoms compared to the atoms below the surface of the particle. [3] By extending this to bulk materials, one can see there are nearly no atoms on the surface as compared to the rest of the material.

There are two main types of catalysis; heterogeneous and homogeneous catalysis. On the macro scale, these refer to the states of matter of the catalysts and the reactants. In homogeneous catalysis, both the catalyst and the reacting chemicals are in the same phase. In heterogeneous catalysis, the catalyst is in a different phase than the reactants (i.e. the solid platinum catalyst converting the gaseous CO into CO_2 in automobiles). An advantage of heterogeneous catalysis is the ease of separation of the catalyst from the products. One of the disadvantages of this method is the relatively low selectivity as compared to homogeneous catalysis.[12] If one could improve the yield of a catalyst while still being able to remove it from the chemicals it was assisting, that catalyst would be invaluable. Nanocatalysts are perhaps the best option for achieving this.

While these definitions of homo- and heterogeneous catalysis are useful for most catalysts, they fail to truly account for all of the characteristics of nanocatalysts. Initially all nanocatalysts were defined as heterogeneous catalysts, but this led to confusion.[2] Nanocatalysts have some properties that would be classified as heterogeneous in bulk catalysts (i.e. having several different active sites) while also possessing characteristics that would be identified as homogeneous.

For nanocatalysts, hetero- and homogeneous catalysis refers to where the reaction occurs in relation to the particle itself, not the reaction medium. In heterogeneous nanocatalysis, the reaction occurs on the surface of the nanoparticle. However in homogeneous nanocatalysis, part of the nanoparticle comes off the and the reaction occurs in the surrounding media. The small part of the nanocatalyst is then brought back to the bulk nanocatalyst. This is now the standard definition used by the International Union of Pure and Applied Chemistry (IUPAC).[1]

One effect of homogeneous catalysis with nanoparticles is nanoparticles with sharp

corners (i.e. cubes and cages) have a tendency to become rounded over time as a result of valency unsatisfied atom on the corners and edges dissolve into the solution. This leads to homogeneous catalysis but as the atoms disappear and atoms on the faces are less active than the corners, this causes a loss in the activity of the catalyst over time.[19]

Having a solid understanding of how these nanocatalysts work to improve reactions is non-trivial. However, it is very difficult to discern the true nature of the mechanism of the nanocatlysts. A rounding effect does not confirm a homogeneous catalysis, nor does it disprove heterogeneous catalysis. In fact, many times it is not even clear whether it is the nanoparticles that have been the catalysts as opposed to the metal salt precursor used to create particles such as platinum nanotetrahedra and nanocubes.[19]

Activation energy (E_a) is the preferred value to examine the effect of a catalyst on a reaction. E_a is the amount of energy needed to overcome in order to allow the reaction to proceed, as shown in Figure 2.
By reducing the amount of energy needed to allow the reaction to proceed, more reactions are likely to occur per unit time, which in turn increases the conversion of the reactants to products. E_a is determined by using the Arrhenius equation:

$$k = Ae^{(-Ea/RT)}(1)$$

where k is the rate constant, A is the preexponential factor, typically expressed in s^{-1}, E_a is the activation energy (in kJ/mol), R is 8.31 kJ/mol K, and T is the temperature in K. This equation can be manipulated to show a direct relationship between the change in rate against the temperature, where the slope is activation energy (multiplied by R).

$$lnk = lnA - (Ea/R)(1/T)(2)$$

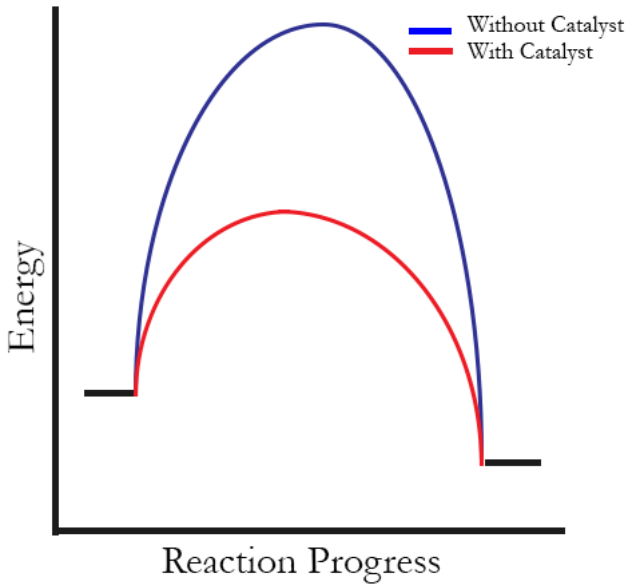

Figure 2: Diagram showing E_a with and without a catalyst.

Therefore, by determining the rate of a reaction at several different temperatures and plotting the rate constant, k, against those temperatures, the activation energy can be determined. The same batch of catalyst solution can be divided into several aliquots, one used for each temperature measurement, therefore the concentration does not need to be determined.

The confinement effect is a possible area in which nanocages may further enhance the overall rate of the reaction. Some experimental results suggest that reactants may become trapped inside a nanocage. Once trapped, these reactants would collide more frequently and interact with each other. This would not have any effect on E_a, but it would increase k by increasing A. The preexponential factor, A, is also known as the collision frequency factor, as it determines the number of collisions of reactants per second. In limiting the amount of space the reactants have (and having that area surrounded by active catalyst), more reactions should, in principle, take place.

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CHAPTER II

POLYSTYRENE AS AN INERT SUPPORT STRUCTURE

2.1 Abstract

Nanocatalysis is an emerging field within the greater division of nanotechnology. Nanocatalysts have improved activity over bulk models, but have some current difficulties that may be reduced, or even eliminated. One of these problems is the loss of the nanocatalyst that makes it hard to recycle and reuse the nanoparticles in subsequent reactions. By finding a nonreactive material on which nanoparticles can easily be adsorbed or attached, the catalysts can be easily reused. However, some of the materials that have been used as support structures in the past have shown some catalytic activity on their own. An alternative material is then needed to replace these common supports. Polymers hold great promise because of their largely inert properties. Polystyrene was chosen due to its ability to swell and contract, which can be used to envelop the nanocatalysts and ensure they are more easily reused. Platinum nanocubes were used in the reduction of 4-nitrophenol via borohydride. The polystyrene was shown to have zero contribution to the catalysis and function as a successful inert substrate.

2.2 Introduction

While nanocatalysts have tremendous advantages over standard bulk catalysts, one issue that presents a significant drawback is the ability to pull these particles out of solution[12]. Standard attempts to centrifuge the solution can result in aggregation of the nanoparticles, reducing their effectiveness[2]. Support structures are used to easily recycle nanoparticles. Common inert supports include aluminum and silica, though they are occasionally active in reactions.[8] It is therefore beneficial to find other supports that are inert and can be used in those reactions.

Polymers, such as polystyrene, are typically inactive in reactions and can be used as supports.[6, 10] However, there have not been many studies of these materials in catalytic reactions. Polystyrene microspheres in particular are potentially desirable as a support structure due to their small size and ability to load nanoparticles onto the surface.[10] Polystyrene is a simple aromatic polymer, the structure is shown below. It is very resistive to both acids and bases[11], which makes it ideal for a wide variety of catalytic reactions, many of which could take place under a range of pHs.

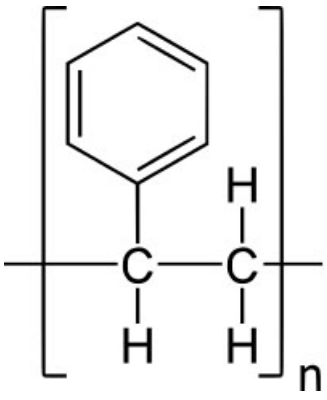

Figure 3: Chemical Structure of Polystyrene

Additionally, polystyrene has the ability to swell in the presence of tetrahydrofuran (THF), and shrink in the absence of it.[7] This is beneficial for easily loading

nanocatalysts onto polystyrene without chemically altering either the catalyst or the support. Many other support structures either require a linker or need to be chemically modified to successfully adsorb the catalyst onto them.

Reducing aromatic nitrocompounds, such as nitrophenol and nitrobenzene, is of economic interest. These compounds are frequently either produced as by-products or needed in production of dyes, pesticides, and pharmacological studies. In particular, 4-aminophenol is a required intermediate in the synthesis of drugs such as acetaminophen.[4] Given the large quantities of acetaminophen produced (on the order of 30,000 tons per year), there is a tremendous incentive to synthesize 4-aminophenol as efficiently and effectively as possible.[1] Metals in acid are commonly used currently, however that procedure results in a toxic metal oxide byproduct. A reaction environment that is both pH neutral and limited in the byproducts it creates would reduce the overall cost of the operation.

The reduction of 4-nitrophenol with sodium borohydride has been studied previous by Zeng et. al. They have found that the activation energy using their catalyst (hollow Au nanoparticles) is between 28 and 55 kJ/mol, depending on how hollowed out the nanoparticles were.[13]

Platinum is among the most commonly used metals for catalysis. Among the industrial uses for platinum are the oxidation of carbon monoxide to carbon dioxide by catalytic converters in cars[5], degradation of azo dyes in waste treatment[9], and petroleum cracking[3]. Due to the high cost of platinum, it is very important to maximize the catalytic activity by ensuring as much of the platinum is actually being used in catalysis. One of the best ways to be sure of this is to use a nanocatalyst. This will reduce the amount of material and will maximize the surface area : volume ratio. Furthermore, there are more active sites on the nanocatalyst than on bulk catalysts.

By reducing 4-nitrophenol in a safe, cheap manner, a whole industry of chemical syntheses can profit. While platinum is not inexpensive, being able to use all of it (or nearly all of it), and being able to recycle the catalyst would reduce costs over using a bulk material. Polystyrene can assist in maximizing the reusability of the nanoparticles in its role as a support system. This means the nanoparticles can be recycled and reused, improving the cost : use ratio. Using nanoparticles instead of bulk materials means more platinum is actually doing the work instead of remaining inert under the surface. Combining these two ideas should ensure a safe, effective, and simple means of accelerating this reaction.

2.3 Experimental

Platinum nanocubes were prepared by reducing platinum salt in the presence of sodium borohydride. Trimethyl ammonium bromide (TTAB, 3.3 g) was added to 80 mL of water at 50 °C. After five minutes, potassium tetrachloroplatinate (10 mM; 10 mL) was added to the solution and allowed to dissolve. Sodium borohydride (0.32 M; 10 mL) was then contributed to the flask and the flask was covered with a septa. A needle was poked through the septa to allow the hydrogen gas byproduct to escape. After 15 minutes, the needle was removed and the solution was allowed to sit overnight. The solution was centrifuged at 3,000 rpm for 30 minutes and the supernatant was kept. It was then centrifuged again, this time at 13,000 rpm for 5 minutes.

The nanocubes were then loaded onto polystyrene microspheres. Polystyrene will expand in the presence of THF and contract once the THF is removed as shown in the schematic below. Specifically, 1.4 mL of polystyrene microspheres were added to a vial followed by the platinum nanocubes (10 mL). THF (3 mL) was the added to the solution, causing the polystyrene to swell. The solution was stirred using a rotovac, which allowed the THF to evaporate over a span of 20 minutes. The solution was centrifuged for 5 minutes at 14,000 rpm three times, with the supernatant being kept each time.

The reduction of 4-nitrophenol to 4-aminophenol with sodium borohydride was studied at 25, 30, 35, and 40 °C. A UV-Vis spectrum was taken every 5 minutes for approximately an hour and the peak at 420 nm was monitored. This was done both with colloidal nanoparticles and the nanoparticles loaded onto the polystyrene microspheres. 4-nitrophenol (30 μL; 2 mM) was added to a cuvette with 100 μL of catalyst. Ice cold sodium borohydride (2 mL; 0.06 M) was added to the solution and the reaction monitored.

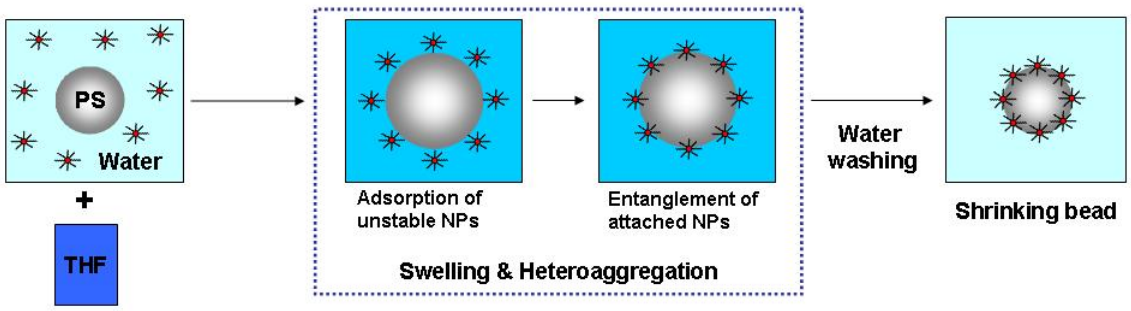

Figure 4: Schematic of process of loading platinum nanocubes onto polystyrene microspheres

A mixture of polystyrene microspheres and unloaded platinum nanocubes was also prepared to investigate the effect of having the two particles in solution on the catalysis. Colloidal platinum nanocubes (60 μL), were added to 1.67 mL of water in a cuvette. Polystyrene microspheres (100 μL) were then added to the solution, followed by 4-nitrophenol (30 μL; 2 mM), and the placed in a water bath at the above mentioned temperatures. After five minutes, ice-cold sodium borohydride (2 mL; 0.06 M) was added to the solution and a UV-Vis spectra was taken every five minutes.

Potassium tetrachloroplatinate, trimethyltetradecylammonium bromide, 4-nitrophenol, and sodium borohydride were purchased from Sigma Aldrich. Polystyrene microspheres were purchased from Duke Scientific Corp. A Cary 500 UV-Vis spectrometer was used to take the spectroscopic measurements, a JEOL 100CX transmission electron microscope was used to determine the size and shape of the platinum nanoparticle, while a Zeiss 60 scanning electron microscope were used to verify the loading of the platinum onto the polystyrene.

2.4 Results & Discussion

TEM images (Figure 4A) show the nanocubes have sharp corners when they are initially synthesized and have 20 nm edge length. However, once the particles have been used as a catalyst in the reduction of 4-nitrophenol, there is clear rounding of the corners (Figures 4B-E). This has been documented in previous studies using solid nanoparticles with clearly defined corners. Frequently, the corners will be used in the reaction as catalytic sites and then the atoms will move to a different part of the nanoparticle. Over time, this can cause the nanocube to lose some of its effectiveness as it will be composed of more side atoms and fewer corner and edge atoms, which are more active. While this suggests homogeneous catalysis, it does not confirm it.

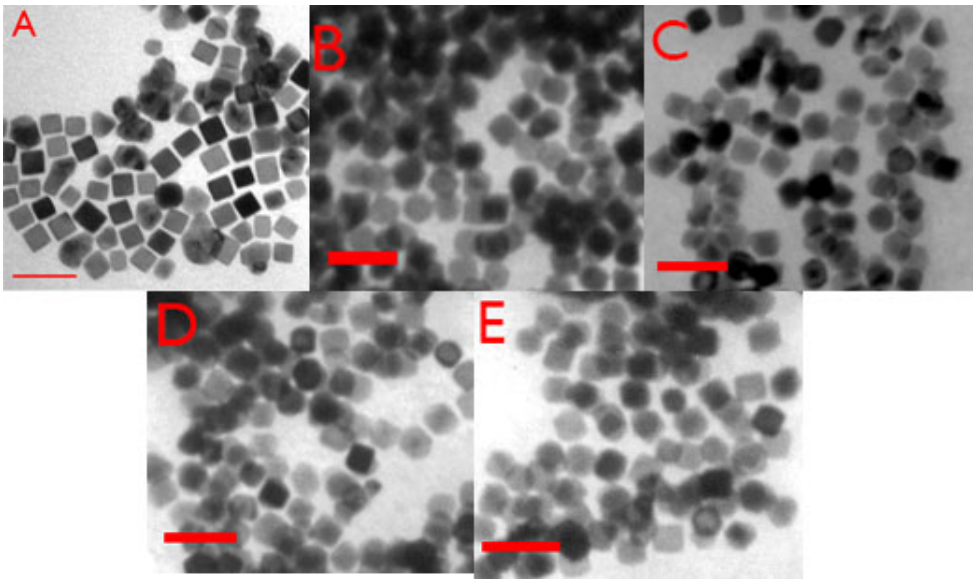

Figure 5: TEM images of platinum nanocubes before (A) and after use in reduction of 4-nitrophenol at 25 °C (B), 30 °C (C), 35 °C (D), and 40 °C (E). Scale bar is 50 nm.

The SEM images (Figure 5) show the particles are covering the polystyrene microspheres. The degradation of the microspheres is due to the electron beam. The polystyrene absorbs the energy of the beam and breaks down while it is being imaged. Despite this degradation of the polystyrene, the cubes can still be seen on the exterior of the microspheres. Especially on the microspheres on the

SEM micrographs on the second half of each image. This provides evidence that the cubes have been successfully deposited on the polystyrene. Furthermore, the polystyrene spheres show no morphological changes when the platinum is added to them.

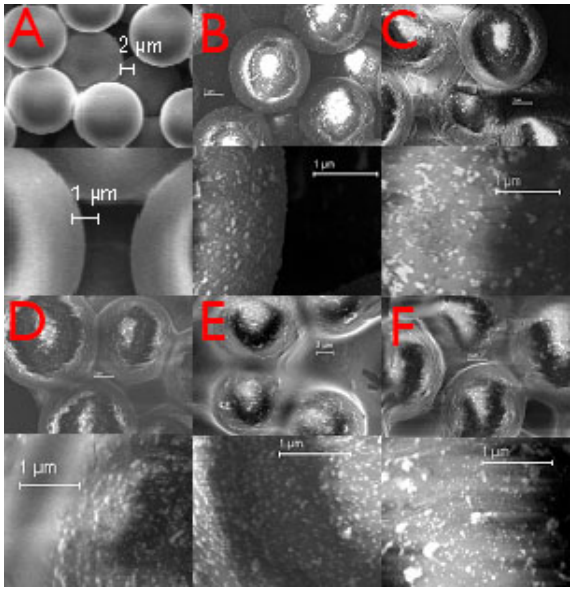

Figure 6: SEM image of polystyrene microspheres before loading (A) after loading (B) with platinum nanocubes and after use in catalysis at 25 - 40 °C (C-F).

The stability of the nanoparticles loaded onto polystyrene were also examined with respect to temperature. A sample of platinum loaded polystyrene microspheres was heated to 60 °C and no changes were found on the SEM images. Therefore, any change in the rate of 4-nitrophenol reduction could not be due to the interactions between the polystyrene and platinum nor the added heat, only with the reaction itself.

Sodium borohydride reduces 4-nitrophenol to 4-aminophenol by removing a pair of hydrogens and replacing them with two oxygens on the nitrogen in the four position. This catalytic reaction was treated as a pseudo-first order reaction, as the ratio of borohydride to 4-aminophenol was very high ($>$ 10:1). Based on a first order reaction, the natural logarithm of the rates was measured against the inverse of the temperature (1000/T; K^{-1})

The rates of the reduction of 4-nitrophenol with borohydride using colloidal particles as a catalyst were -0.037 ± 0.002 (25 °C), -0.048 ± 0.003 (30 °C), -0.053 ± 0.002 (35 °C), and -0.064 ± 0.002 (40 °C), as shown in Figure 6.

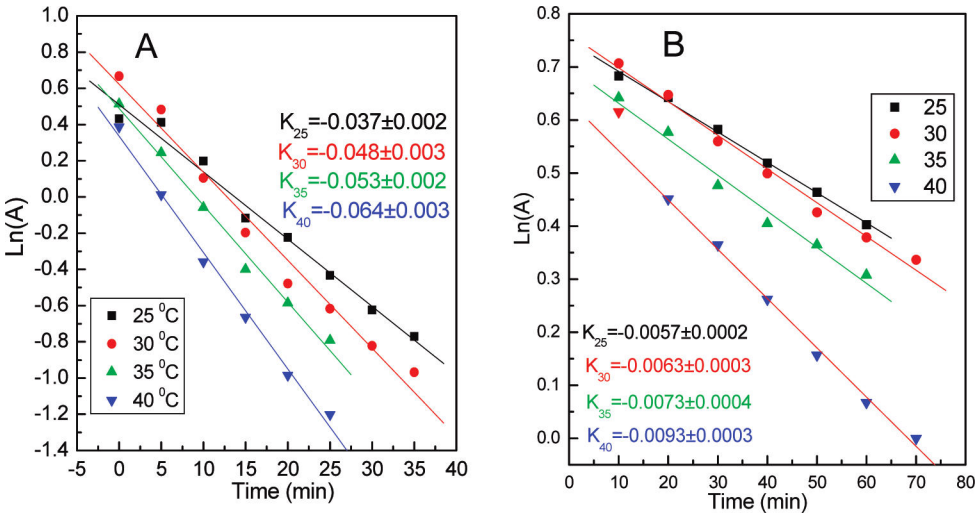

Figure 7: First order rate plots of colloidal platinum nanocubes (A) and platinum nanocubes loaded onto polystyrene microspheres (B) for the reduction of 4-nitrophenol with sodium borohyride.

The reduction of 4-nitrophenol with borohydride can be treated as a first order reaction if the ratio of the two reactants is sufficiently high (4-nitrophenol : borohydride = 1:10). In the case of this experiment, a ratio of 1 : 2000 was used to ensure a first order reaction would occur throughout the experiment. The temperature was not allowed to exceed 40 °C because higher temperatures cause the borohydride to degrade, thus changing the ratio of the two reactants.

The rates of the colloidal particles are approximately seven times higher than those of the nanocubes loaded onto the polystyrene microspheres, despite the activation energies being comparable. This may be due to the steric limitations, such as part of the cubes being covered by the polystyrene. As shown in the Figure 5, when the nanocubes are swallowed up by the polystyrene, there is a loss

of surface area. This may reduce the number of active sites available to the reactants and thus slow the reaction. A second steric hindrance may occur due to the polystyrene itself. The microspheres take up substantially more volume than the platinum nanocubes, but do not appear to be reactive in the solution. This can limit the ability of the reactants to reach the catalyst and create a slower reaction than that with only the catalyst and reactants.

By examining the rates of the colloidal platinum nanoparticles and mapping it against the inverse temperatures studied (Figure 7), an activation energy of 3.3 $\pm$ 0.4 kJ/mol was found. The activation energy for the platinum nanoparticles loaded onto the microspheres was 2.9 $\pm$ 0.4 kJ/mol. Because the activation energies of the two sets of data are comparable, it can be determined the polystyrene does not react with the 4-nitrophenol or the borohydride.

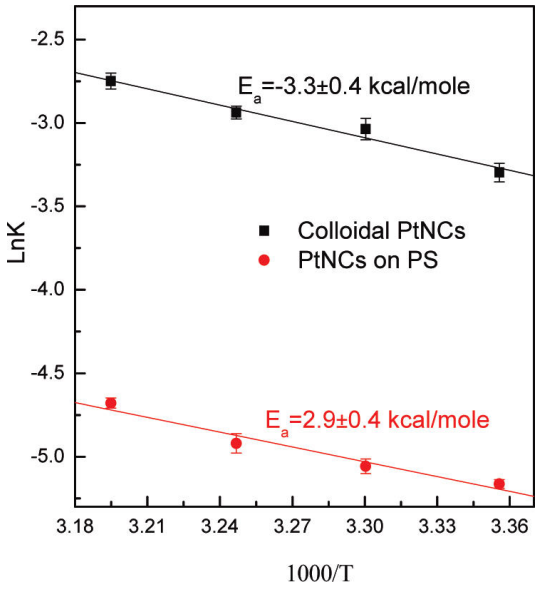

Figure 8: Activation energies of reduction of 4-nitrophenol with borohydride using colloidal nanocubes and nanocubes loaded onto polystyrene microspheres

The similar activation energies show that the polystyrene is truly inert. Therefore,the goal of finding a viable alternative support structure has been achieved. Further work in this area can be focused on determining the effectiveness of polystyrene microspheres with other nanocatalysts (Ag nanocubes, Pt, Pd, &,

Ag nanocages, bimetallic nanocages, etc). Additionally, other reactions should be investigated to determine if this support structure posseses widespread viability or if it is limited to specific reactions. Zhao et. al have shown alumina as a possible catalyst. Therefore, those reactions would make ideal targets to determine if polystyrene microspheres are an effective alternative to alumina.

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CHAPTER III

EFFECT OF METAL RATIO IN BIMETALLIC NANOCAGES ON CATALYSIS

3.1 Introduction

Platinum nanocages have been prepared[8] using a technique called galvanic displacement. [10] In this technique, the template particle (Ag nanocube) metal atoms removed from the interior and fewer metal ions of a 2^{nd} metal in solution are reduced and deposited on a the surface of the cube. In the particular case of synthesizing platinum (or palladium cages or bimetallic cages consisting of platinum (or palladium) and silver, two silver atoms are removed from the Ag nanocube for every palladium (or platinum) ion reduced and deposited on the cube surface. The energy required to reduce Pt or Pd (Pt^{2+} (aq) $\rightarrow 2Pt^{0}$ (s)) is less than $2Ag^{0}$ (s) $\rightarrow 2Ag^{+}$ (aq), thus creating a spontaneous reaction.

Bimetallic nanoparticles have been prepared, usually as core/shell particles.[5, 12, 3, 6, 2] Typically, these particles are synthesized by creating an initial core particle and then coating it with a second material (frequently silica, though metal oxides are often used as well). Shell/shell particles have been prepared by the El-Sayed group, though an in depth study of the formation of these particles has not been investigated.[8] It is believed they are formed via the galvanic displacement technique. While gold nanocages are easily formed due to the large difference in reduction potentials between the template material (Ag) and the gold, platinum and palladium have much lower reduction potentials. $Au^{3}+ \rightarrow Au^{0}$ has a reduction potential of (1.50 eV), $Pt^{2}+ \rightarrow Pt^{0}$ (1.188 eV), and $Pd^{2}+ \rightarrow Pd^{0}$ (0.915 eV), while $Ag^{0} \rightarrow Ag^{+}$ has a reduction potential of 0.7991 eV. It is possible this can affect the degree to which the displacement of silver can take place.

The electron transfer reaction between hexacyanoferrate (HCF) and sodium thiosulfate is a relatively easy reaction to study. The hexacyanoferrate has a sharp peak at 420 nm that degrades as hexacyanoferrate turns into pentacyanoferrate.[1] This allows for UV-Vis spectroscopy measurements to determine the rate of reaction, which are both accurate and easy. Furthermore, because the reaction is in aqueous solution, the catalysts can be dispersed in the solution and mixed in with the reactants. This reaction has been studied by the El-Sayed group using platinum nanoparticles (tetrahedra, spheres, prisms)[9]. Furthermore, oxidizing ferrocyanide is a common way of producing ferricyanide. (Ferricyanide is used in photography[11] and to produce Prussian blue, a common dye.[4])

The mechanism for this reaction has been described by Mahmoud and is shown in the schematic below.[7] A pair of thiosulfates bind to the catalyst (the platinum in this schematic) through the sulfur, forming a Pt-thiosulfate complex. Platinum and gold have been the only metals to be tested with nanoparticles. Once the thiosulfate has bonded to the platinum, a ferrocyanide anion, which began as potassium hexacyanoferride and dissociated in solution, bonds to a platinum particle, which dissolves from the main catalyst and interacts with the thiosulfates. The ferrocyanide ion is then oxidized by the thiosulfide, creating ferricyanide and tetrathionate ions. Afterwards, the platinum is redeposited back on the nanoparticle.

Nanocages are an area of focus due to a couple of factors. There is more surface area in a cage than in a cube of similar dimensions and it is possible for the reactants to be trapped inside the cage, thus increasing the number of collisions and thus the rate of the reaction. Nanocages have been used in catalysis, though they have primarily been monometallic cages. In the very limited number of bimetallic cages studied, it has been shown the exterior metal is not dominantly used in the catalysis.

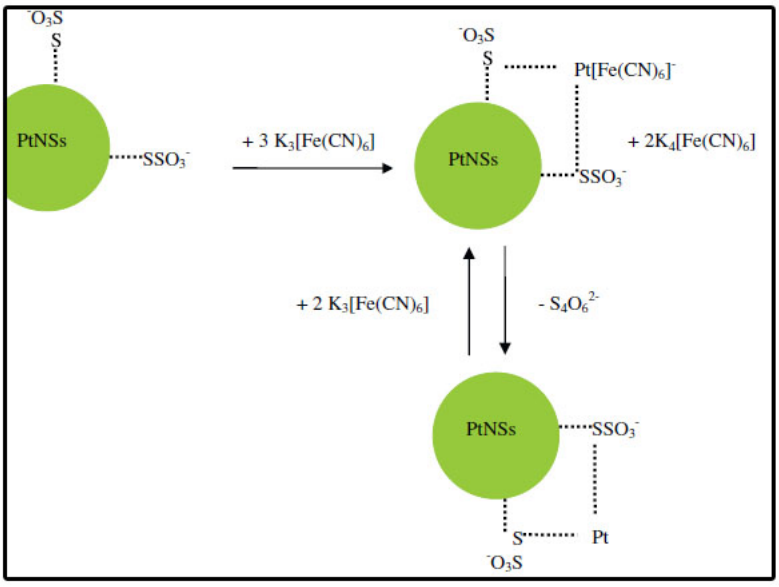

Figure 9: Schematic outlining the electron transfer mechanism of HCF and thiosulfate.

The El-Sayed group has studied platinum-palladium and palladium-platinum nanocages as well as gold-platinum and gold-palladium.[8] The kinetic parameters of the bimetallic cages were compared to monometallic nanoparticles using the same reduction of 4-nitrophenol with sodium borohydride. It was found the activation energy and frequency factors were similar for platinum nanocages and bimetallic nanocages where platinum is the interior metal and similarly palladium nanocages and bimetallic nanocages where palladium was the interior metal. These results suggested that the reaction was taking place inside the nanocage. However, only one type of PtPd nanocage and one PdPt nanocage was studied. The amount of each metal was not investigated nor was a change in those ratios studied. By changing these ratios a difference in the activation energy may be observed.

3.2 Experimental

Silver nanocubes were prepared by heating 35 mL ethylene glycol (EG) for 1 hour at 140 °C with constant stirring. Polyvinylpyrrolidone (MW $\sim$ 55,000; 5 mL; 1.45 mM) was then added and the temperature was increased to 150 °C. After 5 minutes, sodium sulfide (400 μL; 3mM) and silver nitrate (2.5 mL; 0.282 mM) were added sequentially. Stirring was then stopped and the solution was allowed to sit for 5 minutes. Afterwards, stirring was resumed and adjusted until a silver/green color appeared. The plasmon peak was examined using UV-Vis spectroscopy and a peak at $\sim$ 440 nm was found. The cubes were stored in ethylene glycol until needed.

Platinum/silver nanocages were prepared using the silver nanocubes as templates. Initially, the silver nanocubes were spun down using a microcentrifuge at 14,000 rpm for 5 minutes. This was done twice to remove all of the organic compounds and any nitrate ions. Three milliliters of the concentrated cubes were added to 20 mL of deionized water. K_2PtCl_4 (5 mL; 0.12 M) was added in 1 mL aliquots every three minutes. The vial was shaken for the first minute and allowed to sit for the next two minutes. This was done with 5 mL of K_2PtCl_4 with a sample taken out for imaging every minute. These particles were spun down at 14,000 rpm for 5 minutes. Pd/Ag nanocages were prepared using a similar method, with 0.06 M K_2PdCl_4 in place of 0.12 M K_2PtCl_4.

Bimetallic nanocages were preparing using the method described above, but with more control. 40 nm silver cubes were used as a template. 3 mL of centrifuged silver cubes were added to 20 mL of D.I. water. H_2PtCl_4 (mM) or H_2PdCl_4 (mM) was added at different amounts to obtain 5 different ratios of Pt/Ag and Pd/Ag nanocages. Specifically, 1, 3, 5, 7, and 10 mL of platinum and palladium salt were added to the silver cube solution at 3 minute intervals. The solution was then centrifuged twice at 14,000 rpm for 5 minutes. The supernatant was discarded

while the precipitate was kept. These nanocages were then used in catalysis to measure the effect of changing the ratio of the 2 metals (either Pt and Ag or Pd and Ag).

Palladium nanocubes were prepared by initially synthesizing 22 nm palladium nanocubes as seeds and growing them to 40 nm. Palladium nanocubes with an edge length of 22 nm were synthesized by adding 0.5 mL of 10 mM H_2PdCl_4 solution to 10 mL 12.5 mM CTAB. The solution was then heated to 95 °C for 5 minutes and 80 μL of 100 mM ascorbic acid was added as a reducing agent. After 30 minutes, the seed solution was prepared. To prepare 40 nm platinum nanocubes, 5 mL of 50 mM CTAB was added to 125 μL of 10 mM H_2PdCl_4 and heated to 40 °C. Seed solution (300 μL) was added, followed by ascorbic acid (25 μL; 100 mM). The nanocubes were allowed to grow for 14 hours and then centrifuged at 12,000 rpm for 10 minutes. The supernatant was discarded and the precipitate was kept.

The electron transfer reaction between $K_3Fe(CN_6)$ and $Na_2S_2O_3$ was studied because this reaction has been examined with solid platinum nanoparticles in the past, but never with silver particles. This reaction was also carried out with silver and palladium nanocubes for comparison.

A cuvette of catalyst (0.3 mL) and $K_3Fe(CN_6)$ (0.01 M; 0.3 mL) was added to a water bath and stirred for 5 minutes. The spectrometer was blanked with the cuvette and 1.0 mL of sodium thiosulfate (0.1 M) was added to the solution. The cuvette was removed from the water bath and a sample taken every 3-5 minutes. This was repeated for approximately one hour.

3.3 Results & Discussion

Silver nanocubes morphed into nanocages with a Pt exterior and Ag interior by the addition of Pt. Cubes with an edge length of 40 nm grew initially to 60 nm with 1 mL of H_2PtCl_4 and then slowly decreased back to their initial size with the addition of more platinum. The TEM images showing a larger (and rougher) edge length after the initial platinum was added suggests the platinum is added to the outside of the cage, not the interior as previously reported.

This is further confirmed with the UV-Vis spectroscopy that evinces a lack of surface plasmon. If silver was on the exterior of the cage, then a surface plasmon resonance would appear corresponding to silver. The UV-Vis spectroscopy could not be used to gauge the evolution from nanocubes to nanocages because the peak moved very erratically. The initial peak was at $\sim$ 450 nm and only changed between 452 and 475 nm, though it was not a consistent change. Once the platinum-silver nanocages (further noted as PtAg nanocages) were allowed to sit for a several hours, this peak disappeared entirely and only the *d-d* transition peak of the platinum was observed. This peak appears at approximately 260 nm, but is very difficult to measure because the UV-Vis is less accurate below 300 nm.

Once the progression of PtAg nanocages was determined, they were used in catalysis. PdAg nanocages (nanocages with palladium on the exterior and silver on the inside) were expected to evolve in a similar manner as palladium and platinum act in similar ways. The activation energy was examined instead of the rate because an accurate measurement of the catalyst concentration was difficult to obtain. The surface plasmons of platinum and palladium overlap their *d-d* band transitions, which are not in the visible spectra, so the SPR peak cannot be used to determine the optical density. Therefore, concentration was not determined for PtAg or PdAg nanocages.

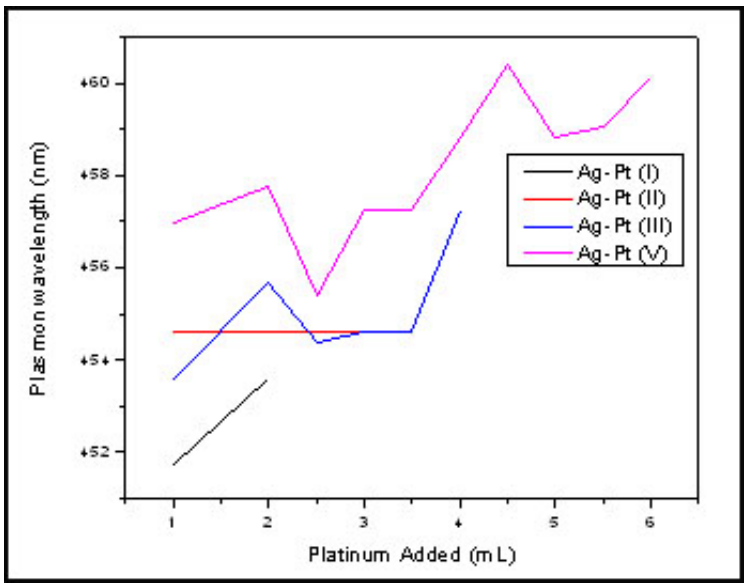

Figure 10: Progression of UV-Vis Absorbance Peaks of Surface Plasmon Resonance as Ag Nanocubes become PtAg Nanocages. Amount of Pt increases from I to V.

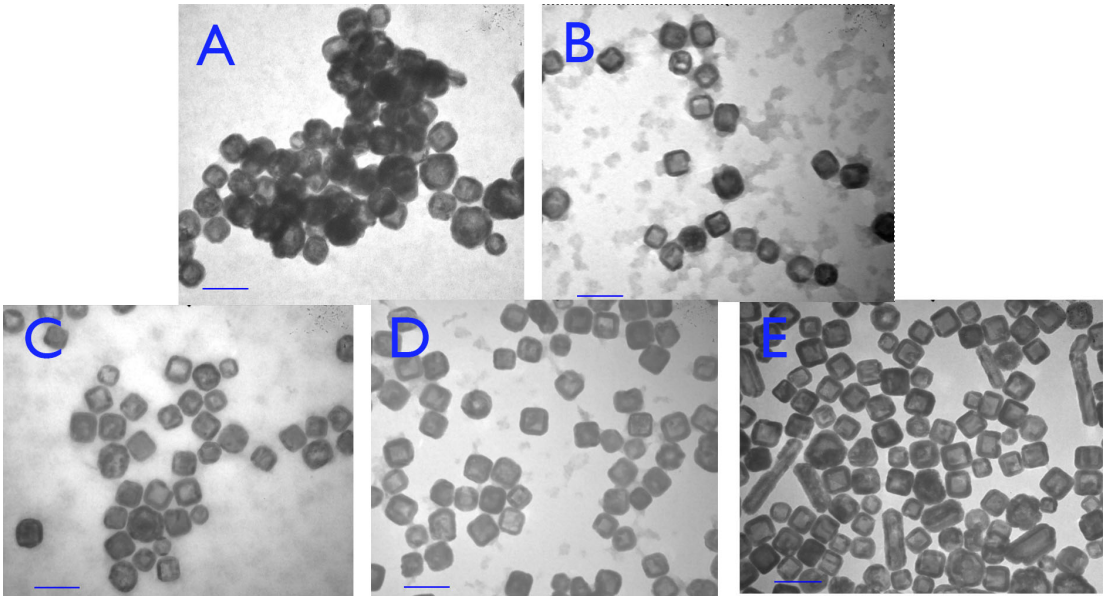

Figure 11: TEM images as the amount of Pt added was increased in Ag Nanocubes. Particles evolve from rough nanoparticles with poorly defined shapes to well defined nanocages with clearly defined edges. A is after 1 mL of K_2PtCl_4, B is after 2 mL of K_2PtCl_4, C is after 3 mL of K_2PtCl_4, D is after 4 mL of K_2PtCl_4, and 5 is after 5 mL of K_2PtCl_4. Scale bar is 100 nm.

The activation energy was determined using the method described in the previous chapter. The inverse temperature was plotted against the natural log of the

rate constants, k, obtained at four different temperatures. E_a for silver cubes was comparable to the control experiment without any catalyst (56.3 kJ/mol vs. 58.2 kJ/mol, respectively). This can be attributed to the silver cubes falling out of the solution as soon as the thiosulfate is added. The silver is rendered inert when the thiosulfate either displaces the PVP on the silver cubes or is added to it. Because this does not occur when silver spheres are used in place of silver cubes capped with citrate, it is suggested that the PVP is removed from the surface of the cubes. If any silver nanoparticles precipitated out of solution when thiosulfate was added to the solution, the spheres (capped with citrate) should do so, but they do not.

This problem was resolved by adding a small amount of platinum or palladium to the exterior of the nanocube using the galvanic displacement technique. Once the particles had a small amount of Pt or Pd, the resulting nanoparticles were dissolved readily in solution. They also remained in solution after the addition of thiosulfate. This allowed the nanocages to successfully be used in catalysis.

PtAg (and PdAg) nanocages were successfully synthesized for the first time using silver nanocubes as templates by utilizing the galvanic displacement method, some of the silver was removed from the nanocubes and platinum (or palladium) was added to the outside of the particle.

By adding platinum to the silver nanocubes, PtAg nanocages were created. Initially, it was suspected that pure platinum nanocages were created, but EDS measurements confirm the presence of silver in the solution (Figure 12). This silver must come from the nanocages and not the presence of silver chloride (which is a byproduct of the galvanic replacement). If silver chloride were present, then chloride would also appear on the EDS measurements. However, only silver, platinum, nitrogen, oxygen, carbon, and copper are observed. Carbon and copper can be attributed to result from the carbon coating and the copper grid of the

sample holders used for the TEM. Nitrogen and oxygen are attributable to the PVP capping agent.

For inductively coupled plasma atomic emission spectroscopy (ICP-AES) the

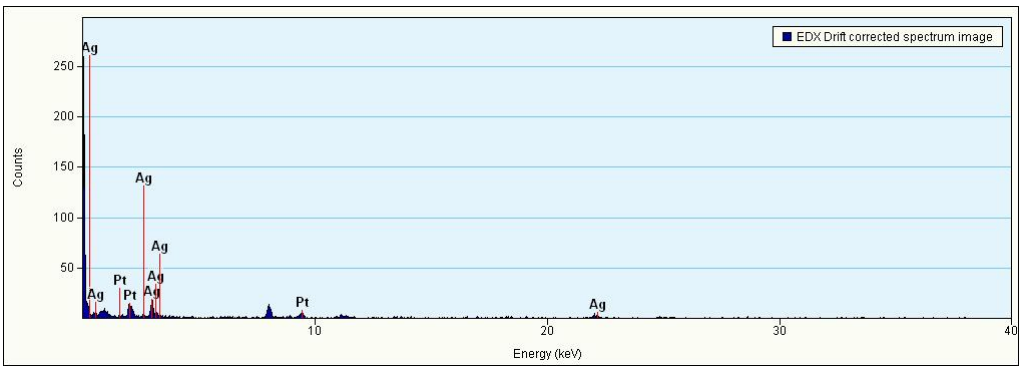

Figure 12: Energy Dispersive Spectroscopy of PtAg nanocages.

nanoparticles were dissolved in a combination of nitric and hydrochloric acids. This could cause chlorine to either attach itself to any remaining silver ions in the solution or simply remain in solution on its own. This would create the appearance of silver chloride in solution and the presence of silver might be dismissed as not part of the cages. However, by using EDS this issue is resolved. The silver must come from the cage itself. Although EDS can detect the silver on the cages as well as free silver ions, silver ions would more than likely not account for the amount of silver present in the image. Additionally, the volume of bimetallic nanocages was very small, so ICP-AES could not accurately determine the metal concentrations, even if the chlorine issue was not prevalent.

As the platinum content in the cages increases, the activation energy also increases. This suggests the silver is the active metal in the catalyst, or there is a synergistic effect between the platinum and silver. The size and number of holes in the cages also increase, which is further evidence the silver is the active metal. If the platinum were more active than the silver, the activation energy should decrease as the platinum content increased. The activation energy is lower than pure

Pt nanocubes, but those nanocubes had an edge length of 7 nm. Pt nanocubes may be better only because of their smaller size.[9]

One interesting result is the increase in the activation energy as the amount of platinum increases. This is particularly interesting because of the low activation energy of platinum cubes. Platinum nanoparticles have been studied, though those particles were significantly smaller. The lower activation energy of the platinum nanoparticles as compared to the bimetallic particles may be due to the higher number of active sites on a smaller particle.

Pt-Ag and Pd-Ag nanocages were tested in this reaction and it was found that with increasing amounts Pt or Pd added the activation energy increased, as shown in Figures 9 and 10.

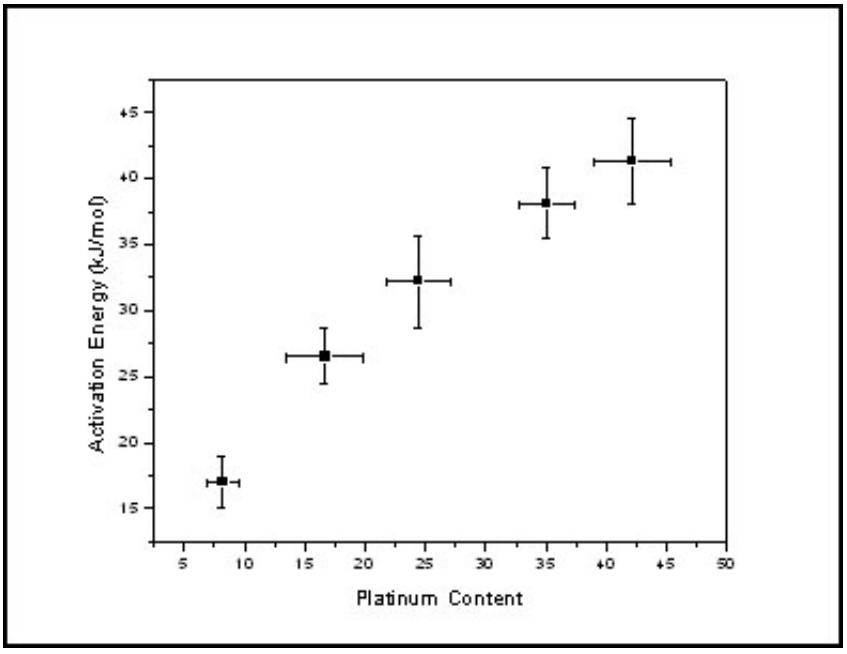

Figure 13: Platinum content of PtAg nanocages vs. Activation Energy.

The additional volume of the second metal (either Pd or Pt) had three effects on the silver nanocubes. The first was that the composition of the nanoparticle changed. Adding more Pt or Pd caused the ratio of Pt (or Pd) to increase from

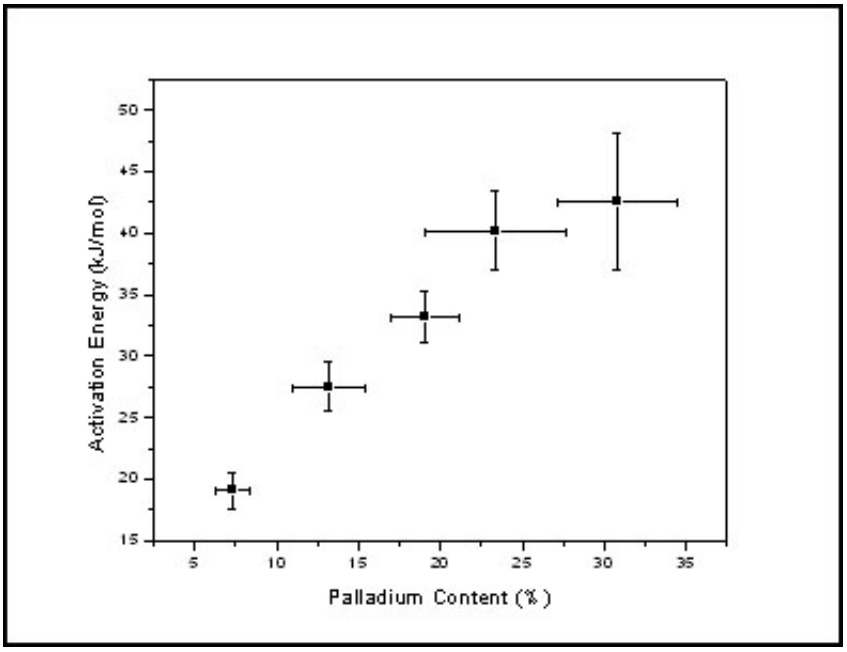

Figure 14: Palladium content of PdAg nanocages vs. Activation Energy.

Platinum Content (%)	Activation Energy (kJ/mol)
0	56.3
8.2 ± 1.3	17.0 ± 1.9
16.7 ± 3.2	26.5 ± 2.1
24.4 ± 2.7	32.2 ± 3.5
35.1 ± 2.3	38.1 ± 2.7
42.1 ± 3.2	41.3 ± 3.2
100	26

0 % to approximately 30-40 % (depending on whether the 2^{nd} metal was Pd or Pt). The second effect of adding more Pt or Pd was a further hollowing effect as compared to smaller amounts of Pt or Pd. It is very difficult, if not possible, to determine which of these is the cause of the change in activation energy. The confinement effect should decrease the activation energy. Lastly, as shown earlier, adding more platinum causes the edges to smoothen. Because catalysts are most effective when they have roughened surfaces with many edges, corners, and defect sites, the smoothing of the nanocage may create a less effective catalyst.

Another important observation is the limit in creating a pure platinum nanocage

Palladium Content (%)	Activation Energy (kJ/mol)
0	56.3
7.3 ± 1.1	19.1 ± 1.5
13.2 ± 2.2	27.5 ± 2.0
19.1 ± 2.1	33.2 ± 2.1
23.4 ± 4.3	40.2 ± 3.2
30.8 ± 3.7	45.4 ± 5.6

from a silver nanocube. Regardless of how much platinum salt was added to the silver cube solution, the platinum content never exceeded 42 %. This may have to do with the reduction potential of $Pt^{2+} \rightarrow Pt^{0}$ as compared to Ag. Reducing platinum requires more energy than oxidizing silver, so it is not necessarily going to completely displace all of the silver. It is also harder to reduce platinum than it is to reduce gold, so while there have been several papers put out using gold nanocages, they cannot necessarily be used to explain how platinum nanocages are formed.

3.4 Conclusion

By adding platinum to pure silver nanocubes, platinum/silver nanocages can be created using the galvanic displacement technique. This occurs by removing some of the silver from the interior and replacing it with platinum on the exterior shell. Initially, the outer coating of platinum increases the size of the cage and as more platinum is added, the size of the cage is reduced back to those of the template cube. While it had been previously thought that pure platinum nanocages were created, it was found silver was discovered in the final particles using UV-vis and energy dispersive spectroscopy. This was also confirmed in created PdAg nanocages.

By adding small amounts of platinum or palladium to the silver nanocubes, three main effects took place. The first was a change in the metal composition of the nanoparticles, starting with 100% silver and dropping to 58% silver and 42% platinum. A similar change was found when adding palladium to the nanoparticles. This allowed the nanoparticles to remain in solution longer in the presence of thiosulfate and could actually be used in catalysis for the reduction of hexacyanoferrate. This addition was limited to about 40 % platinum and 30 % palladium. It is possible this limitation can be attributed to the higher reduction potential of Pt and Pd as compared to Ag. It is also much lower than the reduction potential of Au, which was the first metal used in the galvanic displacement technique.

The second change was a hollowing out of the nanocubes. This took place because Pt and Pd are added via the galvanic displacement technique. Both the platinum and palladium is supposed to form a cage out the silver cubes at a similar rate (due to both metals having an oxidation state of +2 as salts and this reduces two Ag^{+} ions), but the platinum could displace more silver due to its higher reduction potential. The cage formation out could have created a confinement effect in the nanocages which should enhance the catalysis, but was hindered by the addition

of the second, less catalytically active, metal. The nanocage also becomes more smoothed as the 2^{nd} metal is added. This could reduce the catalytic activity by reducing the number of active sites on the nanocage.

Lastly, the addition of these two metals helped to catalyze the electron transfer reaction as compared to the pure silver cubes. The best activation energy of PtAg nanocages was better than silver cubes or silver nanospheres. This suggests that the silver may be more effective than platinum or palladium in catalysis, but needs some of the outer metal to protect from the thiosulfate. Solid platinum nanoparticles have a low activation energy for this reaction (14.0 kJ/mol for tetrahedra). The interaction of these two metals may be creating a destructive effect on each other to create a composite surface.

Bimetallic nanocages on the whole need further study. There may be other reactions in which these particles have a synergistic effect. Other metals may be of interest as well. Because the reduction potential is so low for gold, it is possible that PdAu and PtAu nanocages can be produced in which the gold completely displaces the silver.

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